Adsorption
MRID# 42537802

DATA EVALUATION RECORD

STUDY 1
CHEM 053201 Methyl Bromide §163-1

Both were in OPP.N

FORMULATION--00--ACTIVE INGREDIENT

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study cannot be used to fulfill data requirements.

2. This study is **unacceptable** for the following reasons:

   a. The soils were autoclaved before use, which may have altered the physical properties of the soils and thus influenced the observed behavior of the test substance.

   b. The water added to the equilibration flasks did not contain $CaCl_2$. The water should have contained between 5-20 meq/L $CaCl_2$ as this concentration of Ca^{++} is normally encountered in the field environment. The addition of deionized/distilled water to the soil may have caused some loss of soil-sorbed cations to the aqueous addition, which may have, in turn, affected the adsorption process.

c. In the control flasks that contained methyl bromide-treated water but no soil, 1.3-25.6% of the applied methyl bromide was "lost" from the system after 24 hours and 1.7-29.4% was "lost" after 48 hours. This indicates an unacceptable amount of leakage and a poor material balance.

d. No soil samples were analyzed after the adsorption phase of the study to determine whether, in fact, the material that was not in solution or in the air had been adsorbed by the soil. Adsorption was calculated from the measured concentrations of methyl bromide detected in the air and water samples. These calculations were made assuming that there was no loss from the flasks by volatilization, which was in fact, not the case as indicated by the control flasks.

Based on batch equilibrium experiments, methyl bromide (purity >99.5%), at approximately 9, 25, 44, 102, and 251 µg/mL, was determined to be very mobile in sandy loam and sand soil:solution slurries (1:5 ratio) that were equilibrated at an unspecified temperature for 48 hours with stirring (Tables 8-12). After 48 hours of equilibration, the distribution of methyl bromide between the soil and solution phases was 1:0.77 to 1:1.4 in flasks treated at 9 µg/mL, 1:1.7 to 1:3.1 in flasks treated at 25 and 44 µg/mL, and 1:2.2 to 1:7.0 in flasks treated at 102 and 251 µg/mL. At 48 hours, 30-69% of the applied methyl bromide remained in solution and 9-40% had either adsorbed to the soil or been lost.

METHODOLOGY:

Three sandy loam soils and one sand soil (Table 1) were air-dried, sieved (0.5 cm), homogenized, and autoclaved. Subsamples (50 g) of each soil were mixed with aliquots (250 mL) of sterile aqueous solutions containing methyl bromide (purity >99.5%, Linde) at approximately 9, 24, 44, 102, and 251 µg/mL. There was one control without soil for each test concentration. The sample flasks were sealed with plastic caps with a sampling hole covered by a teflon liner; the caps were designed so that air and water samples could be taken without opening the flasks. The soil:solution slurries were stirred magnetically for 48 hours at an unspecified temperature. At 24 and 48 hours posttreatment, the stirring was interrupted, the soil was allowed to settle, and air and water samples were taken for analysis. After the 48-hour sampling, the soil and solution phases were separated by centrifugation and the solution was removed from the flasks.

In order to determine desorption, the soil pellets from the adsorption portion of the study were mixed with 200 mL of pesticide-free water, and returned to the original flasks. The flasks were capped, and the soil:water slurries stirred magnetically for 48 hours. Air and water samples were collected at 24 and 48 hours as described above. After the 48-hour sampling, the soil and solution phases were separated by centrifugation, and the soil pellets collected for analysis.

Air samples were diluted with air and analyzed directly for methyl bromide using GC with electron capture detection. Water samples were diluted with acetonitrile and filtered prior to analysis for methyl bromide using GC. The soil samples were mixed with water and heated, and the distillate vapors containing methyl bromide were collected in cooled toluene. The toluene was dried over anhydrous sodium sulfate prior to analysis by GC. Methyl bromide concentrations in the air, water, and soil were determined by comparison to standard curves developed using methyl bromide standards dissolved in air or toluene. Recovery efficiencies ranged from 79 to 89% from soil fortified with methyl bromide at 62 ppm.

DATA SUMMARY:

Based on batch equilibrium experiments, methyl bromide (purity >99.5%), at approximately 9, 25, 44, 102, and 251 µg/mL, was determined to be very mobile in sandy loam and sand soil:solution slurries (1:5 ratio) that were equilibrated at an unspecified temperature for 48 hours with stirring (Tables 8-12). The soils had been autoclaved before use. Adsorption of methyl bromide to the soils did not appear to be related to the clay content, organic matter content, or CEC. The distribution of methyl bromide between the soil, solution, and air phases did appear to be concentration-dependent; the proportion of the applied methyl bromide that had volatilized or been adsorbed by the soil (or lost from the system, since adsorption could not be distinguished from loss) decreased as the concentration in the initial solution increased. After 48 hours of equilibration, the distribution of methyl bromide between the soil and solution phases was 1:0.77 to 1:1.4 in flasks treated at 9 µg/mL, 1:1.7 to 1:3.1 in flasks treated at 25 and 44 µg/mL, and 1:2.2 to 1:7.0 in flasks treated at 102 and 251 µg/mL. At 48 hours, 30-69% of the applied methyl bromide remained in solution and 9-40% had either adsorbed to the soil or been lost. After 48 hours of equilibration, volatilized methyl bromide was 40-51% of the applied in flasks treated at 9 µg/mL and 22-34% in those treated at 25-251 µg/mL.

Following a single 24-hour desorption in pesticide-free water, 89-96% of the soil-adsorbed methyl bromide had been desorbed (Tables 14-23). Between 3.4 and 12.8% of the applied methyl bromide remained adsorbed to the soil. At the end of the desorption portion of the experiment, the material balances ranged from 70 to 89% of the applied. In control flasks that contained methyl bromide-treated water but no soil, 1.3-23.6% of the applied methyl bromide was "lost" from the system after 24 hours and 1.7-29.4% was "lost" after 48 hours (Table 7).

COMMENTS:

1. Desorption was determined from the 24- rather than 48-hour data because equilibrium had been established by 24 hours. At 48 hours, the concentration of methyl bromide was equal to or less than the 24-hour value. The study authors suggested that the decreases resulted from methyl bromide leaking from the sample flasks.

2. Much of the data were presented in term of "total µg in the air, soil, or solution". The data were recalculated in terms of "% of the applied" by the reviewer: µg of methyl bromide in the air, soil, or solution at 48 hours were divided by initial concentration of methyl bromide in solution.

3. Freundlich K_{ads} and K_{des} values were not calculated.

4. The temperature at which the study was conducted was not reported.

5. The soils described by the study authors as Canfield, Holly, and Wooster silt loam soils are sandy loam soils according to the USDA Soil Textural Classification System. The soils are described as sandy loams in this report.

TABLES/FIGURES

FILE 49002.6

Table 1. The characterics of the four soils used in the study. All soils were obtained in Ohio. The Canfield collection was taken from an open field on the WIL Research facility. The Holly collection was taken near the Jerome Fork of the Mohican River. The Wooster soil was taken from a woodlot near Havesville.

Soil	Soil type	Moisture content	Soil Composition			Organic content
			Sand	Silt	Clay	
		(%)	(%)	(%)	(%)	(%)
Canfield	Silt loam	2.0	56.0	36.0	8.0	5.5
Holly	Silt loam	1.6	69.0	28.5	2.5	7.4
Wooster	Silt loam	2.4	59.0	34.0	7.0	7.2
Agricultural Sand	Sand	0.0	100.0	0	0	0.3

FILE 49002.5

Table 7. The distribution of methyl bromide in the control flasks where soil was not added.

Experiment Number	Time	Amount of MBr at zero time	Amount of MBr in the air	Amount of MBr in the water	Apparent loss of MBr from the flask	
	(hr)	(ug)	(ug)	(ug)	(ug)	(%)
1	24	2265	627	1106		
			648	1081	534	23.6
	48	2265	719	914		
			706	859	666	29.4
	72	2265	775	898		
			732	898	614	27.1
	96	2265	613	1138		
			573	1111	548	24.2
2	24	6200	2310	3681		
			2310	3681	209	3.4
	48	6200	1477	3302		
			1422	3362	1418	22.9
	72	6200	1164	3451		
			1190	3641	1477	23.8
	96	6200	1058	2604		
			1086	2495	2578	41.6

FILE 49002.5

Table 7, cont. The distribution of methyl bromide in the control flasks where soil was not added.

Experiment Number	Time	Amount of MBr at zero time	Amount of MBr in the air	Amount of MBr in the water	Apparent loss of MBr from the flask	
	(hr)	(ug)	(ug)	(ug)	(ug)	(%)
3	24	11100	3322	6705		
			3278	6785	1055	9.5
	48	11100	3413	5754		
			3413	5831	1894	17.1
	72	11100	2490	6875		
			2581	6629	1812	16.3
	96	11100	2535	6019		
			2579	6103	2482	22.4
4	24	25620	7740	17201		
			7816	17815	334	1.3
	48	25620	6414	18581		
			6490	18896	430	1.7
	72	25620	6071	18364		
			5995	18660	1075	4.2
	96	25620	5464	15903		
			5540	16257	4038	15.8

FILE 49002.5

Table 7 cont. The distribution of methyl bromide in the control flasks where soil was not added.

Experiment Number	Time	Amount of MBr at zero time	Amount of MBr in the air	Amount of MBr in the water	Apparent loss of MBr from the flask	
	(hr)	(ug)	(ug)	(ug)	(ug)	(%)
5	24	62750	17885	40830		
			18338	39961	4243	6.8
	48	62750	17163	36720		
			17378	33723	10258	16.3
	72	62750	15232	38457		
			15662	39293	8428	13.4
	96	62750	18116	35747	8995	14.3
			17901	35747		

FILE 49002.5

Table 8. The distribution of methyl bromide during the adsorption phase of experiment #1 where the concentration of MBr in the original solution was 9.06 ppm. The total amount of methyl bromide in each flask at time zero was 2,265 ug.

Flask Number	Time	Amount of MBr in the air	Amount of MBr in the water	Total amount in air and water	Amount adsorbed on soil or lost*
	(hr)	(ug)	(ug)	(ug)	(ug)
26-2B	24	997	1069	2022	243
		971	1008		
	48	612	914	1575	690
		633	991		
26-2C	24	533	838	1400	865
		542	887		
	48	569	826	1351	914
		569	738		
26-2D	24	567	899	1514	751
		602	960		
	48	698	660	1391	874
		730	694		
26-2E	24	584	1166	1784	481
		602	1215		
		816	826	1648	617
		827	826		

*Original amount in the flask (2,265 ug) minus the amount in the air and water at the time indicated.

FILE 49002.5

Table 9. The distribution of methyl bromide during the adsorption phase of experiment #2 where the concentration of MBr in the original solution was 24.80 ppm. The total amount of methyl bromide in each flask at time zero was 6,200 ug.

Flask Number	Time	Amount of MBr in the air	Amount of MBr in the water	Total amount in air and water	Amount adsorbed on soil or lost*
	(hr)	(ug)	(ug)	(ug)	(ug)
33-1B	24	2290	3332	5565	635
		2335	3173		
	48	1738	3362	5081	1119
		1760	3302		
33-1C	24	2313	3554	5618	582
		2290	3078		
	48	1509	2972	4481	1719
		1509	2972		
33-1D	24	2448	3681	6006	194
		2425	3459		
	48	1372	2732	4114	2086
		1303	2822		
33-1E	24	1774	3396	5219	981
		1841	3427		
	48	1280	3062	4361	1839
		1258	3122		

*Original amount in the flask (6200 ug) minus the amount in the air and water at the time indicated.

FILE 49002.5

Table 10. The distribution of methyl bromide during the adsorption phase of experiment #3 where the concentration of MBr in the original solution was 44.4 ppm. The total amount of methyl bromide in each flask at time zero was 11,100 ug.

Flask Number	Time	Amount of MBr in the air	Amount of MBr in the water	Total amount of MBr in air and water	Amount adsorbed on soil or lost*
	(hr.)	(ug)	(ug)	(ug)	(ug)
59-3B	24	2741	7351	9834	1266
		2630	6947		
	48	2591	6298	8872	2228
		2478	6376		
59-3C	24	2518	6301	8658	2442
		2518	5978		
	48	2365	5442	7826	3274
		2403	5442		
59-3D	24	2741	6139	8865	2235
		2630	6220		
	48	2478	6064	8756	2344
		2516	6453		
59-3E	24	2630	7432	9962	1138
		2593	7270		
	48	2478	6453	9009	2091
		2478	6609		

*Original amount in the flask (11,100 ug) minus the amount in the air and water at the time indicated.

FILE 49002.5

Table 11. The distribution of methyl bromide during the adsorption phase of experiment #4 where the concentration of MBr in the original solution was 102.48 ppm. The total amount of methyl bromide in each flask at time zero was 25,620 ug.

Flask Number	Time	Amount of MBr in the air	Amount of MBr in the water	Total amount of MBr in soil and water	Amount adsorbed on soil or lost*
	(hr.)	(ug)	(ug)	(ug)	(ug)
63-3B	24	6598	18737	25610	10
		6535	19351		
	48	5868	16062	22339	3281
		5742	17006		
63-3C	24	6154	19351	25537	83
		6218	19351		
	48	5678	17322	23409	2211
		5552	18266		
63-3D	24	6218	19351	25478	142
		6344	19044		
	48	5363	15747	21173	4447
		5489	15747		
63-3E	24	6091	17508	23752	1868
		6091	17815		
	48	4921	17322	21928	3692
		4921	16692		

*Original amount in the flask (25,620) minus the amount in the air and water at the time indicated.

FILE 49002.5

Table 12. The distribution of methyl bromide during the adsorption phase of experiment #5 where the concentration of MBr in the original solution was 251.0 ppm. The total amount of methyl bromide in each flask at time zero was 62,750 ug.

Flask Number	Time	Amount of MBr in the air	Amount of MBr in the water	Total amount in air and water	Amount adsorbed on soil or lost*
	(hr)	(ug)	(ug) Ce	(ug)	(ug)
86-3B	24	14385	33880	49758	12992
		14764	36486		
	48	12376	33723	46759	15991
		12197	35222		
86-3C	24	15142	35617	51628	11122
		15142	37355		
	48	13453	38219	50922	11828
		13453	36720		
86-3D	24	15142	37355	52252	10498
		15521	36486		
	48	13991	36720	52015	10735
		14350	38969		
86-3E	24	15332	39092	54424	8326
		15332	39092		
	48	14350	39718	53302	9448
		15067	37470		

*Original amount in the flask (62,750) minus the amount in the air and water at the time indicated

FILE 49002.8

Table 14. The distribution of methyl bromide during the desorption phase of experiment #1 where the concentration of MBr in the original solution was 9.06 ppm. The total amount of methyl bromide in each flask at the beginning of the adsorption phase (zero time) was 2265 ug.

Flask Number	Time	Amount of MBr in the air	Amount of MBr in the water	Total amount of MBr desorbed from soil*
	(hr)	(ug)	(ug)	(ug)
26-2B	24	15**	21**	36
		14**	21**	
	48	15**	11**	26
		15**	11**	
26-2C	24	84	125	213
		82	135	
	48	75	111	197
		75	133	
26-2D	24	92	146	254
		93	177	
	48	88	122	215
		87	133	
26-2E	24	93	156	252
		89	166	
	48	88	156	238
		89	144	

*The total amount in the air and water
**The flask was found to have a major leak

FILE 49002.8

Table 15. The distribution of methyl bromide in the desorption phase of experiment #2 where the concentration of MBr in the original solution was 24.80 ppm. The total amount of methyl bromide in each flask at the beginning of the adsorption phase (zero time) was 6,200 ug.

Flask Number	Time	Amount of MBr in the air	Amount of MBr in the water	Total amount of MBr desorbed from the soil*
	(hr.)	(ug)	(ug)	(ug)
33-1B	24	309	546	864
		304	570	
	48	292	498	794
		288	509	
33-1C	24	313	485	815
		322	510	
	48	297	463	769
		292	486	
33-1D	24	251	376	641
		242	413	
	48	204	324	540
		204	347	
33-1E	24	123	170	283
		115	158	
	48	102	197	304
		102	208	

*The total amount in the air and water

FILE 49002.8

Table 16. The distribution of methyl bromide in the desorption phase of experiment #3 where the concentration of MBr in the original solution was 44.4 ppm. The total amount of methyl bromide in each flask at the beginning of the adsorption phase (zero time) was 11100 ug.

Flask Number	Time	Amount of MBr in the air	Amount of MBr in the water	Total amount of MBr desorbed from the soil*
	(hr)	(ug)	(ug)	(ug)
59-3B	24	262	406	681
		262	432	
	48	270	415	668
		264	388	
59-3C	24	279	498	777
		279	498	
	48	270	401	675
		264	415	
59-3D	24	326	498	813
		332	471	
	48	298	548	816
		292	495	
59-3E	24	163	275	438
		151	288	
	48	152	281	426
		152	268	

*The total amount in the air and water

FILE 49002.8

Table 17. The distribution of methyl bromide in the desorption phase of experiment #4 where the concentration of MBr in the original solution was 102.48 ppm. The total amount of methyl bromide in each flask at the beginning of the adsorption phase (zero time) was 25620 ug.

Flask Number	Time	Amount of MBr in the air	Amount of MBr in the water	Total amount of MBr desorbed from the soil*
	(hr.)	(ug)	(ug)	(ug)
63-3B	24	692	1096	1778
		673	1096	
	48	673	1237	1834
		663	1096	
63-3C	24	848	1303	2166
		848	1333	
	48	780	1343	2164
		790	1414	
63-3D	24	712	1096	1808
		682	1126	
	48	692	1060	1765
		682	1096	
63-3E	24	292	563	840
		292	533	
	48	312	530	842
		312	530	

*The total amount in the air and water

FILE 69002.8

Table 18. The distribution of methyl bromide in the desorption phase of experiment #5 where the concentration of MBr in the original solution was 251 ppm. The total amount of methyl bromide in each flask at the beginning of the adsorption phase (zero time) was 62750 ug.

Flask Number	Time	Amount of MBr in the air	Amount of MBr in the water	Total amount of MBr desorbed from the soil#
	(hr)	(ug)	(ug)	(ug)
86-3B	24	1847	3143	4915
		1764	3076	
	48	1690	2860	4564
		1718	2860	
86-3C	24	1073##	2140##	2991
		1030##	1739##	
	48	345##	1215##	1560
		345##	1215##	
86-3D	24	3304	5751	9278
		3347	6153	
	48	3192	5290	8676
		3149	5720	
86-3E	24	2231	3210	5616
		2446	3344	
	48	2243	3432	5496
		2243	3074	

#The total amount in the air and water
##flask leaked

Table 19. Summary of the desorption phase of experiment #1. The amount of MBr in the soil after 48 hrs of the desorption phase was measured directly. The total amount of MBr at the beginning of the desorption phase was calculated by the sum of the amount of MBr on the soil at 48 hrs and the amount of MBr desorbed in 24 hrs (Table 14).

Flask number	Total MBr on the soil measured directly at the end of desorption	Total MBr on the soil at the beginning of the desorption phase	The amount of MBr desorbed from the soil in 24 hrs
	(ug)	(ug)	(%)
26-2B*	3.06 3.45	39*	92
26-2C	24.10 27.35	238	89
26-2D	33.22 29.31	285	89
26-2E	16.93 19.54	270	93

*The flask was found to have a major leak.

Table 20. Summary of the desorption phase of experiment #2. The amount of MBr in the soil after 48 hrs of the desorption phase was measured directly. The total amount of MBr at the beginning of the desorption phase was calculated by the sum of the amount of MBr on the soil at 48 hrs and the amount of MBr desorbed in 24 hrs (Table 15).

Flask number	Total MBr on the soil measured directly at the end of desorption	Total MBr on the soil at the beginning of the desorption phase	The amount of MBr desorbed from the soil in 24 hrs
	(ug)	(ug)	(%)
33-1B	43.82 41.00	906	95
33-1C	52.30 53.72	868	94
33-1D	52.30 52.30	693	92
33-1E	11.31 11.31	294	96

File 49002.9

49002.9

Table 21. Summary of the desorption phase of experiment #3. The amount of MBr in the soil after 48 hrs of the desorption phase was measured directly. The total amount of MBr at the beginning of the desorption phase was calculated by the sum of the amount of MBr on the soil at 48 hrs and the amount of MBr desorbed in 24 hrs (Table 16).

Flask number	Total MBr on the soil measured directly at the end of desorption	Total MBr on the soil at the beginning of the desorption phase	The amount of MBr desorbed from the soil in 24 hrs
	(ug)	(ug)	(%)
59-3B	35.11 35.11	716	95
59-3C	46.82 48.49	825	94
59-3D	75.24 80.26	891	91
59-3E	21.74 25.08	461	95

Table 22. Summary of the desorption phase of experiment 84. The amount of MBr in the soil after 48 hrs of the desorption phase was measured directly. The total amount of MBr at the beginning of the desorption phase was calculated by the sum of the amount of MBr on the soil at 48 hrs and the amount of MBr desorbed in 24 hrs (Table 17).

Flask number	Total MBr on the soil measured directly at the end of desorption	Total MBr on the soil at the beginning of the desorption phase	The amount of MBr desorbed from the soil in 24 hrs
	(ug)	(ug)	(%)
63-3B	112.79 119.42	1894	94
63-3C	172.50 165.87	2335	93
63-3D	172.50 159.23	1974	92
63-3E	46.44 53.08	890	94

49002.9

Table 23. Summary of the desorption phase of experiment #5. The amount of MBr in the soil after 48 hrs of the desorption phase was measured directly. The total amount of MBr at the beginning of the desorption phase was calculated by the sum of the amount of MBr on the soil at 48 hrs and the amount of MBr desorbed in 24 hrs (Table 18).

Flask number	Total MBr on the soil measured directly at the end of desorption	Total MBr on the soil at the beginning of the desorption phase	The amount of MBr desorbed from the soil in 24 hrs
	(ug)	(ug)	(%)
86-3B	243.01 248.80	5161	95
86-3C	92.58 92.58	3084	97#
86-3D	607.53 567.03	9865	94
86-3E	237.23 219.87	5844	96

#The flask was found to have a major leak

1.23 1